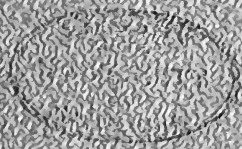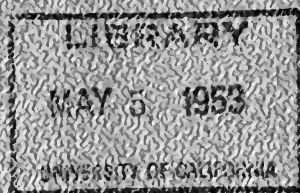# ELECTRICAL CONDUCTIVITY AND VISCOSITY

OF SOME

FUSED ELECTROLYTES

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Electrical Conductivity and Viscosity

of some

Fused Electrolytes

INAUGURAL-DISSERTATION

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Introduction and Work of Previous Investigators

When an electric current passes through a conductor of the second class the acceleration which the potential gradient tends to give the moving ions is offset by the retardation they suffer due to their friction with the medium in which they move. Hence a uniform velocity results, which for a given condition of temperature, pressure and concentration depends only upon the kind of ions and upon the surrounding medium. Consequently it is not improbable that some functional relation might be found to exist between the electrical conductivity of an electrolyte and its fluidity. For the case of aqueous solutions a large amount of investigation has been carried out in this connection, and whether or not we accept the interpretation of the results as satisfactory, at least there is an abundance of data, both for conductivity and viscosity. Kohlrausch[1]) has sketched out a new view of the mechanics of electrolysis, according to which the moving ion carries with it a mass of adhering solvent, and the electrical resistance of an ion he considers as a frictional resistance which increases with the dimensions of the atmosphere surrounding it. The velocity of the

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[1]) Royal Society Proc.—Feb. 1903.

ions will depend then, upon the viscosity of the medium through which they pass, and upon the size of the ionic atmosphere; the conductivity of the solution will depend upon the viscosity of the medium, the size of the ionic atmosphere, and the fraction of dissociated ions in the solution. The same writer long since has shown [1]) that the resistance of an ion expressed in mechanical units must be of the same order of magnitude as the mechanical internal resistance of a molecule. Kohlrausch [2]) and independently Hosking,[3]) based upon his measurements of the change of conductivity and viscosity with the temperature, have both come to the interesting conclusion that at approximately $-36°$ Centigrade, both the specific molecular conductivity and the fluidity, for all solutions, become zero. In general, for aqueous solutions the fluidity increases more rapidly than the conductivity with rising temperature. These and a number of other interesting results have been largely discussed, but as yet no simple relation has been found between these two quantities, and I think it may be said that a satisfactory explanation of the connection between them has not been given.

For the other group of conductors of the second class the matter stands very differently. The following is a list of all the papers describing quantitative measurements of the conductivity of fused electrolytes :—

F. Braun   Pogg. Ann. d'Phys.   Bd. 154   1875
W. Kohlrausch Wied   „   „   „   17   1882

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[1]) Göttinger Nachrichten, 1879, I.
[2]) Sitg. Akad. Wiss. Berlin, Oct. 1901.
[3]) Phil. Mag. (6) 7 May 1904.

Foussereau	Ann. de Chim. et d'Phys (6)		5	1885
E. Bouty and L. Poincaré	„ „ „ „ „ „		17	1889
A. Grätz	Wied Ann. d'Phys.	Bd.	40	1890
Lorenz & Sculze	Zeitschr. f. anorg. Chem.	„	20	1899

A comparison of these papers shows a decided lack of agreement in the values obtained. As examples, the recorded values of the specific conductivity reckoned in reciprocal ohms for the following salts are:—

Lead Chloride at 530°

Braun	2,69
Poincaré	1,66
Grätz	3,19

Potassium Nitrate at 350°

Braun	0,697
Foussereau	0,725
Poincaré	0,724
Grätz	0,747

Sodium Nitrate at 350°

Braun	1,25
Foussereau	0,641
Poincaré	1,302

In the case of lead chloride the disagreement is about 100 %, and in the case of the nitrates Foussereau and Poincaré do not even agree as to which is the better conductor. A careful review of all the work cited above may be found in Lorenz' "Elektrolyse geschmolzener Salze", II. Teil, where the author points out that the variations are largely due to inappropriate methods of correcting for or of preventing polarization.

Furthermore, the wide disagreement in the melting point of the salts as given in these researches indicates either impure salts or inaccurate temperature measurements. The experimental difficulties in these measurements are enormously increased over similar measurements with solutions, owing to the high temperature[1] at which the measurements have to be carried out, but any such differences as are shown above are out of the question.

Fused electrolytes have the advantage of homogeneity over solutions, and Lorenz[2] has shown that they obey Faraday's laws. For these reasons they are particularly interesting for an intimate study of the internal mechanism of electrolytic conductivity. Foussereau concludes from his data in the paper cited above, that the specific resistance of every salt is directly proportional to its coefficient of internal friction for all temperatures. If this conclusion were valid it would be of the greatest interest and importance, but it is to be questioned whether the present state of the data on the electrical conductivity of fused salts warrants any conclusions; even more is this true of the data on internal friction, for which Foussereau's data is all there is in the literature. His measurements were made by the Pouisseuille-Hagenbach method where the reliability of the measurements depends upon the relative dimensions of the capillary, in comparison with the pressure applied.[3] Foussereau makes so little mention of these values, that an estimate of the precision of his results

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[1] Between 300 and 600 degrees Centigrade.
[2] Die Elektrolyse geschmolzener Salze, II. Teil.
[3] For a discussion of this see pp. 26.

can hardly be made. However he does make a temperature correction which I have shown to be superfluous [1]) and which vitiates his results to that extent. Furthermore his measurements have only been made over a considerable temperature range for sodium and potassium nitrates, and these salts are so similar that general conclusions could scarcely be drawn.

Thus the data for electrical conductivity and viscosity of fused electrolytes leaves much to be desired. Aside from its high theoretical interest it is of great importance technically. The purpose of this work then, was to develop a method, and to make a series of measurements of specific electrical conductivity and of viscosity, for a number of fused salts, such that they may be relied upon to a high degree of accuracy, and to draw such conclusions as the data affords. The idea was to make a large series of independent measurements of the same salt, confining the measurements to a few salts whose melting point, chemical constitution, condition of hydration, etc., are such that the only errors likely to be contained in the results are pure experimental ones, rather than to extend the work over a greater range under far less favorable conditions.

[1]) See pp. 44.

Method and Apparatus

General Method

In this work a few normal pieces of apparatus each bearing a certificate of the Physikalisch-Technischen Reichsanstalt in Charlottenburg, were assumed to be as indicated upon these certificates. These pieces of apparatus were :—

1) A normal Weston element,
2) A thermometer (mercury),
3) A platinum, platinum-iridium, thermo-element,
4) Electrical resistance coils.

Furthermore the value of the specific conductivity of sulphuric acid at 18°, and its temperature coefficient over a small interval near 18° were used, as given in the tables of Kohlrausch and Holborn "Leitvermögen der Elektrolyte", and the mean value of all the determinations of the viscosity of water at 13° as given in Landolt-Börnstein-Meyerhoffer-Tabellen, 3. Auflage, was assumed to be correct. None of these could possibly introduce an error of 0,1 %, and no other assumptions were made.

The specific conductivities were calculated from resistances measured by the usual Wheatstone bridge method. Alternating current from an induction coil was used to avoid polarization, and a specially devised electrode holder and capillary tube was employed to offord the proper dimensions for a good minimum.

This cell was calibrated before each set of measurements in the usual manner with a known solution of sulphuric acid. The entire cell was placed within an electric oven containing the melted salt, the temperature of which could he regulated by means of an appropriate rheostat placed in series with it. The temperature was measured by comparing the electromotive force of a thermo-element placed within the melt, with that of a standard Weston element, by measuring the current due to each through the same circuit by means of a sensitive D'Arsonval galvanometer. The thermo-element bearing the Reichsanstalt certificate was placed in the same melted salt with the thermo-element used, and both simultaneously compared with the Weston element to get the temperature calibration curve.

The viscosity measurements were made by the Pouisseuille-Hagenbach method, great pains being taken to have the capillary of such dimensions that all corrections were eliminated.[1]) The method consisted in comparing the time of flow of the same volume of fused salt and of water through the same capillary tube under exactly the same conditions except that of temperature. The ratio of these time intervals is the ratio of the specific viscosity of the salt at its temperature, to that of water at its temperature. That the corrections for the change in dimensions of the apparatus due to the difference in temperature between salt and water eliminate each other, is shown later, when the details of the measurements are considered. The viscosity of water has been accurately determined for all room tem-

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[1]) The value of the measurements depends upon the degree in which this is accomplished. See pp. 36 et seq.

peratures so that from the above measurements the viscosity of the salt can be calculated. It only remained to show that the apparatus is so dimensioned that it gave the correct absolute value for water. This test was made with each piece of apparatus used.

The details of all the above will be considered later under appropriate headings.

Apparatus in Detail

Conductivity Measurements

The Electric Oven

The conditions which a suitable oven must fulfil are —
1) It must be capable of rising to temperature of 600 °
in a conveniently short time. 2) It must be capable of
regulation to maintain any temperature up to 600 °,
constant to within a degree or two, for about fifteen
minutes. 3) It must be capable of construction in suit-
able dimensions. 4) It must have a reasonably long life.

A series of ovens heated by spraying the flames
of a number of powerful gas burners upon them were
tried and found unsatisfactory. Electric ovens, that is,
ovens maintained by the Joule heat of a coil of wire
were tried, with various kinds and dimensions of wire,
and the only one fulfiling all of the above conditions
is the one to be described. Iron wire for winding the
oven suggested itself, but at such high temperatures
iron oxidizes rapidly and hence has to be often re-
wound. Nickel wire of 2 mms. diameter, heavily covered
with an insulation of asbestos was wound spirally,
covering a hollow cylinder of iron. This was covered
with a few layers of asbestos paper and a thick wall
of insulating clay built about the whole, leaving open
only the top. Within the iron cylinder, and separated
by a thin layer of asbestos, fitted a glass or porcelain
vessel in which the salt was to be fused. In the con-

ductivity experiments this vessel had an inside diameter of 45 mms. and a depth of 170 mms., while in the viscosity experiments requiring a broader vessel, the diameter was 110 mms. and the depth 120 mms. When in operation the top was covered by asbestos boards. The oven was operated by an alternating current at 50 volts, and consequently the wire was wound bifillarly. In series with the oven was placed a rheostat and an ammeter. The total resistance of the oven and lead wires was about 1 ohm, so that the maximum current possible was 50 ampères. Hence by inserting more and more resistance at the rheostat, the current could be regulated to any value between 50 and 0 ampères. By studying the current in terms of the temperature, which was observed by the thermo-element galvanometer circuit, the thermo-element being within the oven, the current could be regulated to maintain any temperature up to 600° for more than fifteen minutes, without fluctuating more than 1,5°. As will be seen, it was necessary to maintain constant temperatures only in the viscosity measurements as the conductivity measurements were made by a series of readings as the melt gradually cooled off. With only a fair outside insulation 30 [a] will fuse lead chloride, melting at about 500° within ten minutes. Thus the current was more than sufficient for the purpose.

The Cell

All the fused salts investigated are good conductors, that is, they have a specific conductivity of the magnitude of from 10 to 100 times as great as their water solutions at room temperatures. Furthermore, the usual

form of cell due to Arrhenius, with platinized electrodes is not available, as the platinum black is immediately attacked by the fused salts. Ordinary platinum electrodes are not attacked so far as could be detected. This was tested by leaving a sheet of platinum for thirty minutes in melted lead chloride at 600^0. The platinum showed no signs of being attacked and weighed identically 0,3052 gms. before and after. Silver electrodes were immediately dissolved. The quartz and glass used for the cell were subjected to a similar test and with like results. The diameter of the electrodes which can be used, is limited by the possible dimensions of the oven capable of having a constant temperature throughout. Kohlrausch has found, "Leitvermögen der Elektrolyte" 1898 pp. 11, that for ordinary electrolytes, blank electrodes can be employed to give a good minimum with the Wheatstone bridge-inductorium-telephone method, if the surface of the electrode equals

$$S > \frac{2500}{w} \text{ cm}^2$$

where w is the resistance of the cell in ohms. He considers such results reliable to withen 0,1 %. My experiments show that a faultless minimum can be obtained with fused electrolytes between unplatinized electrodes, with a surface only approximately $1/10$ of that corresponding to the above formula. A simple calculation shows that corresponding to this, with electrodes 22 mms. in diameter, such as were used, and with lead chloride having a specific conductivity approximately 2,0 reciprocal ohms, a column of electrolyte 500 cms. in length would be necessary. Since the length is restricted to about 5 cms. by other considerations, or $1/100$ of the

above, it is evident that to accomplish the desired result the diameter of cross section of the column must be reduced to $\sqrt{1/100} \times 22$ mms., or 2,2 mms. Capillary tubes of about this diameter were employed.
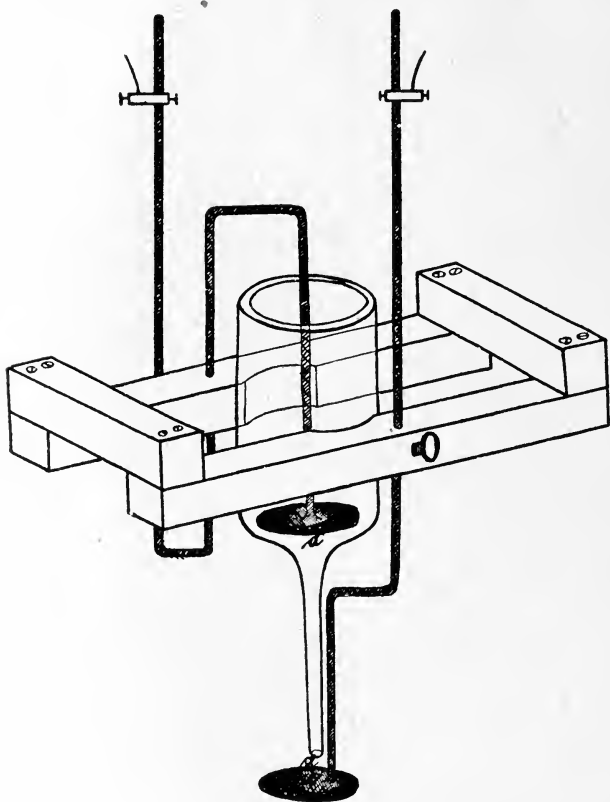

Fig. 1

The construction and arrangement is as follows. The capillary piece was made of Jena hard glass, for the work with the salts of low melting point, and of quartz, for the work with the higher melting bivalent salts. The quartz or glass was shaped and held as

shown in figure 1. The long rectangular bars are of brass and to each an electrode is firmly secured by means of a set screw. These bars are insulated by the short cross-bars which are of stabalite, and the brass bars are long enough so that the stabalite is away from the heat of the furnace. The insulation between the electrodes was tested from time to time, and the resistance of the stabalite always found to be practically infinite. The brass pieces are grooved out to admit the quartz or glass cylinder, which is securely fixed with a set screw, protected with asbestos. The platinum wires of the electrodes are 2 mms. in diameter, and hence stiff enough so that the relative position of the parts remained the same during any one experiment.

The proceedure was to set up the electrodes with capillary as in the sketch, and then to submerge the whole in a tube of standard sulphuric acid, filling the capillary, and covering the upper electrode. It was then made one arm of a Wheatstone bridge, and its resistance measured in the usual way. The acid containing vessel was within a thermostat, and the temperature at the time of the measurement was accurately observed. Several observations were in every case made, and the mean value used. The temperature readings were corrected according to the Reichsanstalt certificate which the thermometer bore. From this data the cell constant, that is the resistance the capillary between the electrodes would have if it contained an electrolyte of unit conductivity, was calculated. Approximately maximum sulphuric and was used, whose exact concentration was determined by density measurements, and the value of its specific conductivity at the temperature, interpolated

from Kohlrausch and Holborn tables. The cell was then removed from the acid, carefully washed with water and dried with alcohol and ether, care being taken not to disturb its dimensions; it was then inserted in the fused salt. This was then made one arm of the bridge and its resistance measured, from which the specific conductivity of the salt could be calculated.

When using glass capillaries, it was necessary to correct for the conductivity through the glass itself at the temperatures of the salt measurements. To ascertain this correction, before use, each capillary was melted together at the end, inserted within the melt, with salt inside it as well, and its resistance measured over the entire range of temperature for which it was to be used. The melted together tip was then removed, and the capillary used. This correction varied from 0.3% at $300°$, to about 1% at $400°$. Even if the correction were only ascertained accurately to within 10%, its effect on the final result would never exceed 10% of 1% or 0.1%. However above $400°$ the glass starts to soften and its conductivity rises rapidly, hence quartz capillary tubes were used. The quartz apparatus sealed at the end and measured in this manner had a resistance of over 10^6 ohms, and consequently corrections for its conductivity need not be made. Of course the conductivity of the capillary measured in this manner is not strictly the same as its conductivity under the conditions of the experiment, due to the different distribution of the voltage in the two cases. However, the entire voltage between the electrodes acts across every part of the glass or quartz in the correction measurement, and hence the conductivity in the experiment can never exceed the correction found.

It should be noticed further, that the particular position in which the cell is placed within the salt is of no consequence. Again, any slight displacement of the electrodes or capillary during the measurements, has a very slight effect. The active column of salt between either electrode and the capillary itself (a fig. 1) has a cross sectional area approximately 30 times as great as that within the capillary. The length of the capillary is about 50 mms., hence an error of 0,1 % means an error of 0,05 mms. in length of the capillary, or a displacement of $30 \times 0,05$ or 0,5 mms. in the electrodes. Such an error is out of the question.

The effect of the change of dimensions of the cell due to the difference in temperature between the calibration with acid at 18^0, and the measurements with salts at 250^0 to 600^0, alone remains to be considered. Evidently the effect of the expansion of the platinum is negligible, because this effects only the broader columns of electrolyte, and not the capillary itself. The expansion of the capillary increasing its length is proportional to the 1st power of the lineal coefficient of expansion of glass or quartz, and tends to increase the resistance. The expansion increasing the cross section of the capillary is proportional to the 2nd power of the lineal coefficient of expansion of glass or quartz, and tends to decrease the resistance. Hence the correction to be applied, is to increase the resistance by the fractional amount $\beta (t_1 - t_2)$, where β is the lineal coefficient of expansion, and $(t_1 - t_2)$ the temperature difference. The value of β for the glass used is 0,000006, and for quartz it is not very different. Hence in the worst case, over a temperature interval of 600^0, the correction

would be $0,000006 \times 600 = 0,0036 = 0,36\ \%$. This correction was made in all the calculations.

The Weatstone Bridge

The bridge was the ordinary slide wire arrangement, a metre in length. The wire was of German silver, and it was carefully calibrated throughout its length. No correction exceeded $0,1\ \%$. Also the resitance box coils were standardized against normal coils, and the proper corrections made throughout the calculations. The current was furnished by a single accumulator cell, supplying a small high frequency induction coil. The frequency of the coil had to be very great for a . distinct minimum, and it is only in this case that polarization is avoided. A very sensitive telephone was selected and care was taken that no readings were made near the ends of the wire. All settings could readily be made within one millimetre.

Temperature Measurements

The temperature of the melted salt at the time of the conductivity measurements was determined by means of a platinum platinum-iridium thermo-element, placed within the salt, and forming part of a circuit as described below. Poggendorf's compensation method could not be used as the measurements had to be very rapidly made. In the circuit (figure 2), Ak. is the accumulator placed directly around a resistance box R consisting of 995^w, 2^w, 2^w and 1^w, or 1000^w in all. From this box then, could be taken $^1/_{1000}$, $^2/_{1000}$, $^3/_{1000}$, $^4/_{1000}$, $^5/_{1000}$ or the whole of the electromotive force across its terminals due to the accumulator, and the amount taken is led to the switches A and B. The central

points of each of these switches leads to a third switch
C; A through a resistance coil W_2 of 10,000^w, and B
through a graphite resistance W_1 of over 10^6 ohms.
W_2 is great enough so that the current through R is
not appreciably effected when the circuit —R-A-W_2-C-Galv
—is closed, around 1^w, 2^w, 3^w, 4^w or 5^w at R. The
central points of C lead to a sensitive D'Arsonval gal-
vanometer. The other terminals of B lead to a standard
Weston element W. E., and those of A to the thermo-
element within the melt.
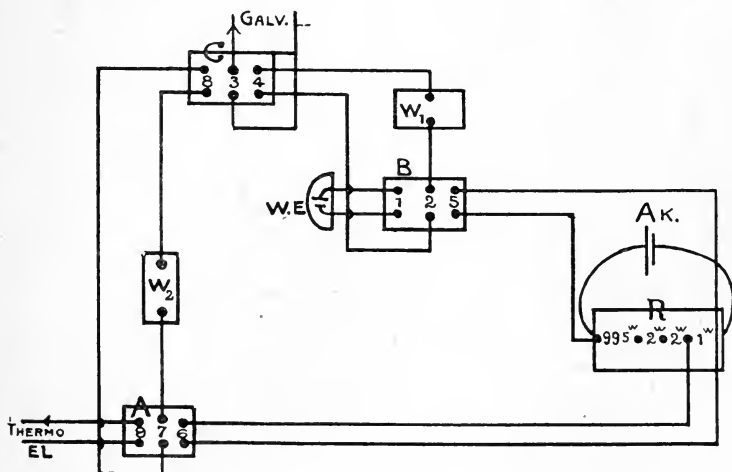
Fig. 2.

The object of this arrangement is clear—the elec-
tromotive force of the thermo-element is to be compared
with that of the standard Weston element—but the
former gives only a few millivolts and the latter a volt,
so that the current due to them could not be sent to
the galvanometer through the same resistance. On the
other hand if the Weston element were placed directly
around R, and in that way only $1/1000$ of its e. m. f.

taken from the 1^w coil, this could be sent through the millivolt circuit A - W_2 - G and compared with the e. m. f. of the thermo-element, but this would draw current from the standard element and ruin it. Hence the accumulator is compared with the Weston element by comparing their deflections through the volt circuit B-W_1-G, that is through the high graphite resistance W_1, and then $1/1000$ part of this measured accumulator e. m. f., is taken from the 1^w coil, to compare with the e. m. f. of the thermo-element, through the millivolt circuit. The complete operation is then as follows:—first the Weston element is inserted, circuit 1-2-4-3-G, and the deflection observed, then the accumulator is inserted, circuit 5-2-4-3-G. If the deflection of the accumulator were 8 cms., and that of the element whose e. m. f. is 1,019, were 4 cms., then the e. m. f. of the accumulator would equal

$$E = \frac{8}{4}\ 1,019 = 2,038$$

except for a small correction to be considered later. Strictly, E is the potential difference around the terminals of the 1000^w resistance box R, which is what is desired. Next the circuit around the 1^w coil of R, through 6-7-8-3-G is closed, whereby the deflection due to 2,038 millivolts is observed. Then the thermo-element deflection through 9-7-8-3-G, may be calculated. If the latter deflection is 8 cms., and the 6-7-8-3-G deflection above, is 6 cms., then the e. m. f. due to the thermo-element at that particular temperature is

$$E = \frac{8}{6}\ 2,038 = 2,717 \text{ m. v.}$$

again except for a slight correction.

This operation was carried out before and after each run, and the results always found to agree, so that the data was at hand to calculate the e. m. f.'s corresponding to the thermo-element galvanometer readings throughout the run, and from these the temperatures. The zero reading of the galvanometer was taken after each reading and used as a correction.

Calculation of the e. m. f.'s in this way makes one serious assumption, namely, that the e. m. f.'s are proportional to the deflections. This could be avoided by always calibrating very near to that deflection which is to be used in the measurements. For instance, if instead of using one Weston element in the comparison with the accumulator in the above example, two of them in series had been used, both deflections would have been approximately 8 cms. and the error introduced in the calculation would be negligable. It was not always possible to do this, and hence a correction had to be applied which I shall hereafter call the correction for scale proportionality. It is the correction which is to be added to the galvanometer reading observed, because the deflections do not increase quite as rapidly as the current. These corrections are all very small, never exceeding a few tenths of a per cent, and are determined as follows. If with the circuit R-6-7-8-3-G, 1^w, 2^w, 3^w, 4^w and 5^w, be successively inserted at R and the deflections noted, they will be found not quite in the proportion $1 : 2 : 3 : 4 : 5$, as they should be were the deflections exactly proportional to the e. m. f.'s. From this data a curve may be drawn, from which all subsequent readings may be corrected. The coils in R showed no correction when standardized.

All measurements with the thermo-element were made with the cold junction at 0°. The thermo-element was calibrated against a standard thermo-element bearing the certificate of the Reichsanstalt, by placing them both in the same melt with their cold junctions in an ice water mixture, so that by throwing a switch either of them could be inserted into the circuit at A,9. Thus readings of the galvanometer were made due to the e. m. f. of each thermo-element at a common temperature. This was done over the entire range of temperatures to be used. The comparison showed the thermo-element used to have the following e. m. f.'s corresponding to the temperatures—

Degrees Centigrade	E. M. F. in millivolts
300	2,24
400	3,16
500	4,13
600	5,13
700	6,16

Both thermo-element wires were inclosed within and isolated from each other, by porcelain tubes within the melt, and by rubber tubes without.

A run consisted in heating the salt to about 100° above its melting point, and then letting it cool very slowly, simultaneous readings of the galvanometer and slide wire being made at minute intervals.

Conductivity; Calculation and Results

The salts used were obtained from various manufacturers, in original packages, labelled "purissimum", and measurements made with salt directly from packages, checked up in each case with measurements made with the salts further purified by recrystalization. The coincidence of the melting points observed, is further proof of the purity of the salts.

Numerical Calculation

A single illustrative calculation will be carried through in detail from the observed data; each of the values in the tables below is the result of a similar calculation. Thus in the 4th run with potassium nitrate (see pp. 27), at a temperature corresponding to a deflection of 8,37, the following data was observed.

G = Galvanometer reading . . . . . 8,37 cms.
N = Zero reading of galv. . . . . . 00 „
1 = length of slide wire on . . . . 578 mms. resistance box side
w = ohms at resistance box 100

The corresponding data with the capillary sealed (pp. 14) is

G	N	1	w
8,37	00	415	5000

The correction to the reading 578 from the slide wire calibration is negligible. The correction to the 100^w resistance coil is $+ 0,2^w$. Hence the total conductivity of the cell is

$$C_1 = \frac{578}{1000-578} \; \frac{1}{100.2} = .01367$$

reciprocal ohms. Of this the part due to the conductivity of the glass is

$$C_2 = \frac{415}{1000-415} \; \frac{1}{5000} = .000142\frac{1}{w}$$

Hence the true conductivity of the salt is

$$C = C_1 - C_2 = .01367 - .00014 = .01353\frac{1}{w}$$

The data for the cell constant for this particular run is—

Specific conductivity of acid $= .7225\frac{1}{w}$ at 18 °, with a temperature coefficient

$$\frac{1}{X_{18} \; acid} \; \frac{dx}{dt} = .0156$$

Observed—

$$temperature = 19{,}5 °$$
$$w = 100$$
$$l = 571$$

From this the specific conductivity of the acid at 19,5 ° is

$$X_{19,5} = .7225 \; (1 + 1{,}5 \times .0156) = .7391\frac{1}{w}$$

and the cell constant is

$$C_u = \frac{571}{1000-571} \; \frac{1}{.7391} = .01797$$

The ratio $\frac{C}{C_u}$ would give the specific conductivity of the salt at the temperature of this measurement, were it not for the expansion of the capillary (see pp. 15—16). For this case the correction $\beta \; (t_1 - t_2)$ is $.000006$ $(382 - 18) = .002$, although the calculation below, to determine the temperature has first to be made before

t_1 is known. Hence we get finally for the specific conductivity [1])

$$X = \frac{.01353}{.01797} \frac{1}{1,002} = .7513 \frac{1}{w}$$

The additional data for the calculation of the temperature is—2 Westons in series, through volt circuit, with a true e. m. f. of $2,\overset{v}{0}38$, gave a deflection of 14,40 cms. The accumulator through the same circuit gave 14,50 cms. These values checked before and after the run. Hence

$$E = \frac{14,50}{14,40} \, 2,038 = 2,\overset{v}{0}53$$

and the e. m. f. around the 1^w coil is 2,053 millivolts. This gave a deflection of 5,75 cms. through the millivolt circuit. Since the scale proportionality correction for $\frac{8,37}{5,75}$ is 0,01 (see pp. 19).

$$E = \frac{8,38}{5,75} \times 2,053 = 2,99 \text{ m. v.}$$

and the corresponding temperature (table pp. 20) is 382 ^{0}.

The values of the specific conductivities of potassium nitrate and the corresponding temperatures, together with the data from which these were calculated, are tabulated below. Each value of X and T (temperature) is the result of a calculation equivalent to the above, although in executing the calculations it was not necessary to pass through all the steps as shown. In the tables the values of G recorded, have already been corrected for the displacement of the zero point, and E has been calculated including the correction for scale proportionality.

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[1]) See column 8, pp. 27.

Potassium Nitrate

First Run

G	E	T	l	w	C_1	C_2	X	t
972	3,482	433	686	100	.02185	$.0_349$	.9003	0
967	3,464	432	685	„	.02174	$.0_348$	.8966	1
960	3,439	429	684	„	.02165	$.0_348$	.8927	2
948	3,396	425	682	„	.02142	$.0^347$	.8832	3
938	3,362	421	680	„	.02123	$.0_342$	.8776	4
926	3,320	416	677	„	.02091	$.0_337$	.8664	5
914	3.276	413	674	„	.02063	$.0_334$	.8559	6
903	3,253	410	671	„	.02033	$.0^331$	.8437	7
870	3,117	396	661	„	.01938	$.0^323$	.8076	10
856	3,068	390	655	„	.01893	$.0_322$	.7889	11
836	2,997	383	649	„	.01846	$.0_316$	.7718	12
823	2,950	375	645	„	.01808	$.0_315$	.7561	13
811	2,905	372	640	„	.01770	$.0_313$	.7412	14
789	2.843	366	632	„	.01712	$.0_310$	.7176	16
780	2,796	360	628	„	.01681	$.0_49$	.7053	17
759	2,720	352	620	„	.01631	$.0_47$	.6847	19
738	2,645	344	610	„	.01561	$.0_46$	.6557	20
729	2,613	340	606	„	.01532	$.0_45$	.6439	21
719	2,577	337	602	„	.01506	$.0_45$	.6330	22
709	2,541	334	598	„	.01483	$.0_45$	.6234	23
708	2,536	333	594	„	.01460	$.0_44$	.6141	24
708	2,536	333	592	„	.01448	$.0_44$	.6089	25
708	2,536	333	592	„	.01448	$.0_44$	.6089	26
707	2,533	333	592	„	.01448	$.0_44$	.6089	27
705	2,527	332	592	„	.04448	$.0_44$	.6089	28
702	2,515	331	591	„	.01442	$.0_44$	.6061	29
700	2,509	330	590	„	.01436	$.0_44$	.5959	30

Cell constant = .02367

Potassium Nitrate

Second Run

G	E	T	l	w	C_1	C_2	X	
881	3,158	400	665	100	.01977	$.0_3 23$	.8124	0
864	3,097	394	661	„	.01938	$.0_3 19$	.7967	1
853	3,057	389	657	‚	.01898	$.0_3 17$	.7807	2
843	3,022	386	653	„	.01870	$.0_3 16$	.7729	3
819	2,936	376	645	„	.01808	$.0_3 13$	.7443	5
807	2,892	371	640	„	.01770	$.0_3 12$	.7276	6
795	2,850	366	636	„	.01742	$.0_3 11$	.7174	7
775	2,778	358	628	„	.01681	$.0_4 9$	.6927	9
763	2,735	354	624	„	.01657	$.0_4 8$	.6825	10
753	2,699	351	619	„	.01623	$.0_4 7$	.6705	11
743	2,663	347	615	„	.01596	$.0_4 6$	.6582	12
722	2,588	337	606	„	.01532	$.0_4 5$	.6323	14
708	2,536	333	598	„	.01483	$.0_4 4$	.6124	16
708	2,536	333	596	„	.01471	$.0_4 4$	.6073	17
708	2,536	333	595	„	.01465	$.0_4 4$	.6059	18
708	2,536	333	595	„	.01465	$.0_4 4$	.6059	19
708	2,536	333	595	„	.01465	$.0_4 4$	.6059	20
708	2,536	333	593	„	.01455	$.0_4 4$	.6010	21
708	2,536	333	592	„	.01455	$.0_4 4$	.6010	22
708	2,536	333	592	„	.01448	$.0_4 4$	.5980	23
707	2,533	333	591	„	.01442	$.0_4 4$	.5957	24
705	2,527	332	589	„	.01450	$.0_4 4$	.5812	25
703	2,520	331	587	„	.01486	$.0_4 4$	.5732	26
700	2,508	330	581	„	.01386	$.0_4 4$	.5732	27
697	2,498	328	567	„	.01307	$.0_4 4$	.5403	28
693	2,484	327	533	„	.01139	$.0_4 3$	.4724	29
690	2,473	326	434	„	.00765	$.0_4 3$	.3160	30

Cell constant = .02407

Potassium Nitrate

Third Run

G	E	T	l	w	C_1	C_2	X	t
920	3,314	**416**	675	100	.02070	$.0_3 35$	**.8426**	0
912	3,285	**413**	673	„	.02052	$.0_3 33$	**.8364**	2
904	3,258	**411**	670	„	.02022	$.0_3 31$	**.8245**	3
893	3,218	**406**	668	„	.02006	$.0_3 28$	**.8193**	4
874	3,148	**399**	663	„	.01960	$.0_3 24$	**.8017**	6
853	3,070	**391**	656	„	.01900	$.0_3 22$	**.7773**	8
830	2,991	**382**	648	„	.01836	$.0_3 19$	**.7520**	10
810	2,919	**374**	641	„	.01778	$.0_3 16$	**.7293**	12
795	2,865	**368** ·	636	„	.01742	$.0_3 12$	**.7162**	$13^{1}/_{4}$
789	2,843	**366**	633	„	.01721	$.0_3 10$	**.7084**	14
763	2,748	**355**	623	„ .	.01650	$.0_4 8$	**.6800**	16
740	2,666	**347**	615	„	.01596	$.0_4 6$	**.6585**	18
731	2,633	**343**	612	„	.01573	$.0_4 6$	**.6486**	19
720	2,594	**338**	606	„	.01532	$.0_4 5$	**.6323**	20
712	3,565	**335**	602	„	.01406	$.0_4 5$	**.6216**	21
706	2,544	**334**	598	„	.01483	$.0_4 5$	**.6120**	22
704	2,536	**333**	596	„	.01471	$.0_4 4$	**.6074**	23
704	2,536	**333**	595	„	.01465	$.0_4 4$	**.6050**	24
704	2,536	**333**	595	„	.01465	$.0_4 4$	**.6050**	25
702	2,528	**332**	594	„	.01460	$.0_4 4$	**.6029**	26
701	2,526	**332**	593	„	.01455	$.0_4 4$	**.6004**	27
699	2,518	**331**	592	„	.01448	$.0_4 4$	**.5986**	28
698	2,514	**330**	590	„	.01436	$.0_4 4$	**.5928**	29
693	2,488	**327**	589	„	.01430	$.0_4 4$	**.5903**	30
690	2,485	**327**	583	„	.01397	$.0_4 4$	**.5765**	31
686	8,472	**325**	568	„	.01322	$.0_4 4$	**.5460**	32
683	2,463	**324**	555	„	.01247	$.0_4 4$	**.5156**	33
680	2,450	**322**	540	„	.00958	$.0_4 4$	**.3960**	34
674	2,428	**319**	301	„	.00430	$.0_4 4$	**.1774**	35
671	2,417	**318**	638	1000	.00176	$.0_4 3$	**.0716**	36

Potassium Nitrate

Fourth Run

G	E	T	l	w	C_1	C_2	X	t
860	3,069	**390**	584	100	.01401	$.0_318$	**.7679**	0
852	3,040	**387**	282	„	.01391	$.0^217$	**.7625**	1
837	2,987	**382**	578	„	.01367	$.0_314$	**.7513**	3
820	2,925	**375**	573	„	.01342	$.0_313$	**.7370**	5
810	2,889	**371**	569	„	.01318	$.0_312$	**.7258**	6
800	2,853	**366**	565	„	.01296	$.0_311$	**.7136**	7
790	2,813	**362**	562	„	.01280	$.0_310$	**.7052**	8
782	2,788	**359**	558	„	.01261	$.0_310$	**.6933**	9
772	2,752	**356**	554	„	.01243	$.0_48$	**.6822**	10
762	2,715	**352**	550	„	.01223	$.0_47$	**.6715**	11
752	2,679	**348**	546	„	.01202	$.0_46$	**.6637**	12
743	2,653	**345**	541	„	.01177	$.0_45$	**.6509**	13
722	2,570	**336**	534	„	.01144	$.0_45$	**.6335**	15
714	2,542	**334**	529	„	.01120	$.0_44$	**.6210**	16
710	2,527	**332**	525	„	.01102	$.0_44$	**.6108**	17
706	2,512	**330**	524	„	.01098	$.0_44$	**.6080**	18
702	2,505	**329**	519	„	.01076	$.0_44$	**.5953**	19
698	2,484	**327**	468	„	.00892	$.8_44$	**.4930**	20
692	2,461	**324**	286	„	.00399	$.0_44$	**.2188**	21
689	2,451	**323**	619	1000	.00163	$.0_43$	**.0888**	22

Cell constant $= .01797$

Potassium Nitrate

Fifth Run

G	E	T	l	w	C_1	C_2	X	t
975	3,449	430	600	100	.01500	$.0_350$	.8790	0
962	3,404	426	596	„	.01471	$.0_348$	.8675	1
953	3,372	422	594	„	.01460	$.0_346$	.8580	2
944	3,341	418	590	„	.01436	$.0_344$	.8520	3
921	3,260	411	584	„	.01401	$.0_334$	.8356	5
910	3,221	406	580	„	.01380	$.0_332$	.8224	6
898	3,180	402	577	„	.01364	$.0_330$	.8110	7
876	3,100	394	569	„	.01318	$.0_325$	.7856	9
841	2,978	381	556	„	.01252	$.0_318$	.7482	12
832	2,945	376	552	„	.01230	$.0_317$	.7360	13
821	2,907	373	547	„	,01208	$.0_315$	.7231	14
797	2,822	363	539	„	.01168	$.0_312$	.7006	16
767	2,715	351	525	„	.01102	$.0_49$	.6620	19
758	2,684	349	521	„	.01086	$.0_48$	.6527	20
748	2,648	344	216	„	.01064	$.0_47$	.6415	21
738	2,613	340	512	„	.01049	$.0_47$	.6315	22
728	2,577	337	207	„	.01027	$,0_46$	.6190	23
720	2,549	335	504	„	.01015	$.0_45$	.6120	24
714	2,528	333	500	„	.00999	$.0_45$	.6030	25
713	2,524	332	496	„	.00982	$.0_45$	.5929	26
713	2,524	332	496	„	.00982	$.0_45$	.5929	27
712	2,520	332	494	„	.00976	$.0_45$	.5900	28
709	2,510	331	410	„	.00693	$.0_44$	.4181	29
707	2,503	330	279	„	.00386	$.0_44$	.2318	30
702	2,485	327	145	„	.00169	$.0_44$	.1001	31
699	2,475	326	430	1000	.00075	$.0_44$	.0431	32

Cell constant $= .01648$

Potassium Nitrate

Sixth Run

G	E	T	l	w	C_1	C_2	X	t
942	3,375	**422**	677	100	.02091	$.0_340$	**.8644**	0
926	3,320	**416**	674	"	.02063	$.0_337$	**.8537**	2
906	3,244	**409**	669	"	.02017	$.0_331$	**.8369**	4
884	3,169	**401**	662	"	.01948	$.0_324$	**.8110**	6
873	3,129	**398**	657	"	.01868	$.0_322$	**.7905**	$7^1/_4$
851	3,049	**388**	651	"	.01862	$.0_317$	**.7778**	9
839	3,008	**384**	646	"	.01816	$.0_315$	**.7589**	10
827	2,965	**379**	641	"	.01778	$.0_314$	**.7433**	11
802	2,875	**369**	633	"	.01721	$.0_311$	**.7314**	13
779	2,792	**360**	622	"	.01644	$.0_49$	**.6894**	15
747	2,676	**349**	609	"	.01554	$.0_46$	**.6522**	18
738	2,646	**344**	605	"	.01526	$.0_45$	**.6407**	19
728	2,606	**340**	601	"	.01499	$.0_45$	**.6297**	20
717	2,570	**336**	597	"	.01478	$.0_44$	**.6212**	21
710	2,544	**334**	593	"	.01455	$.0_44$	**.6115**	22
708	2,536	**333**	591	"	.01442	$.0_44$	**.6059**	23
708	2,536	**333**	591	"	.01442	$.0_44$	**.6059**	24
706	2,530	**332**	590	"	.01486	$.0_44$	**.6034**	25
705	2,527	**332**	581	"	.01356	$.0_44$	**.5823**	26
703	2,520	**331**	563	"	.01285	$.0_44$	**.5399**	27
702	2,518	**331**	539	"	.01168	$.0_44$	**.4900**	28
699	2,504	**330**	494	"	.00976	$.0_44$	**.4099**	29
697	2,498	**329**	477	"	.00910	$.0_44$	**.3826**	30
693	2,484	**327**	387	"	.00630	$.0_44$	**.2638**	31
690	2,473	**326**	210	"	.00265	$.0_43$	**.1100**	32
687	2,462	**325**	420	1000	.00072	$.0_43$	**.0292**	33

Cell constant = .02368

The ninth column gives the time in minutes which have passed since the initial reading, and serves to show the regularity with which the fall in temperature has taken place. It will be noticed that the galvanometer remained stationary at a reading corresponding to about 333 degrees in each run. The time during which it remained stationary depends upon the rate of cooling, and varied in these runs from 3 minutes in the 1st run, to 8 minutes in the 2nd run. The galvanometer readings and the slide wire readings both become constant at the same time, as of course they should, at the melting point of the salt. This removes the objection, that there might be a lag in the recording of temperatures by the thermo-element. Below the melting point the conductivity diminishes very rapidly, but these measurements in the solid state are not reliable, as they depend upon the varying conditions of crystalization etc. This exact method of the determination of the melting point it due to Tamman, and although only incidental to this work, it affords an admirable fixed starting point for each salt from which to tabulate results. Starting with the melting point, the temperature and specific conductivity in reciprocal ohms will be tabulated for each salt at 10° intervals.

Thus for potassium nitrate the six runs give us the following, interpolating over very short intervals where necessary.

333 °

Run	Sp.Cond.	δ
1	.6089	.0029
2	.6059	.0001
3	.6062	.0002
4	.6159	.0101
5	.5929	.0131
6	.6059	.0001
	.6060 mean	.0044 mean

Hence the mean value $.6060\frac{1}{w}$, so for as concordance of results is concerned, has a precision measure of

$$\text{A. D.} = \frac{.0044}{.6060} \frac{1}{\sqrt{6}} = .0030 = 0{,}30\,\%$$

334 °

Run	Sp.Cond.	δ
1	.6532	.0088
2	.6478	.0024
3	.6486	.0032
4	.6471	.0017
5	.6378	.0076
6	.6379	.0075
	.6454 mean	.0052

$$\text{A. D.} = \frac{.0052}{.6060} \frac{1}{\sqrt{6}} = .0034 = 0{,}34\,\%$$

not very different from the first precision measure. And so on for 353 ° — 363 ° — 373 °. In this way, all the results for all the salts have been calculated, and the value of A. D. is always less than 0,38 %. These values were then plotted, conductivities against tempe-

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ratures, giving smooth curves which represented the mean result of all the observations, and from these curves the following tables were read. The more extended tables above will not be given for the other salts. The following are then, the mean values of the specific conductivity in reciprocal ohms as observed, given for $10°$ intervals, commencing with the melting point. $\triangle X$ is the increase in the specific conductivity for the corresponding $10°$.

Potassium Nitrate

T	X	$\triangle X$
333	.6060	
		.0394
343	.6454	
		.0305
353	.6759	
		.0281
363	.7040	
		.0280
373	.7320	
		.0280
383	.7600	
		.0280
393	.7880	
		.0280
403	.8160	
		.0280
413	.8440	

Sodium Nitrate

T	X	$\triangle X$
308	0,965	
		.057
318	1,022	
		.043
328	1,065	
		.043
338	1,108	
		.043
348	1,151	
		.044
358	1,195	
		.044
368	1,239	
		.044
378	1,283	
		.044

T	X	$\triangle X$
388	1,327	
		.044
398	1,371	
		.045
408	1,416	
		.045
418	1,461	

Potassium Bichromate

T	X	$\triangle X$
397	.1959	
		.0239
407	.2198	
		.0183
417	.2381	
		.0182
427	.2563	
		.0182
437	.2745	
		.0182
447	.2927	
		.0182
457	.3109	
		.0182
467	.3291	
		.0182
477	.3473	
		.0182
487	.3655	
		.0182
497	.3837	
		.0182
507	.4019	

Lead Chloride

T	X	$\triangle X$
498	1,395	
		.083
508	1,478	
		.066
518	1,544	
		.052
528	1,596	
		.049
538	1,645	
		.047
548	1,692	
		.046
558	1,738	
		.045
568	1,783	
		.043
578	1,826	
		.040
588	1,866	
		.038
598	1,904	
		.037
608	1,941	

Lead Bromide

T	X	$\triangle$ X
372	.5397	
		.0718
382	.6115	
		.0364
392	.6479	
		.0363
402	.6842	
		.0360
412	.7202	
		.0355
422	.7557	
		.0343
432	.7900	
		.0339
442	.8239	
		.0331
452	.8570	
		.0330
462	.8900	
		.0320
472	.9220	
		.0310
482	.9530	
		.0305
492	.9835	

Viscosity Measurements

Pouisseuille's [1]) method for the measurements of the specific viscosity of fluids, consists simply in forcing a known volume of fluid through a fine capillary tube under a known constant pressure, and measuring the time required. He found that with a capillary of sufficient length the formula

(1)
$$V = \frac{1}{\eta} \frac{\pi}{8} \frac{P}{L} R^4 t$$

was true, where V is the volume of fluid flowing through the capillary in the time t under the pressure P, where R and L are respectively the radius and length of the capillary, and where η is a constant depending upon the fluid. The value of η for water has been thoroughly investigated at all room temperatures. Hence if the volume V of water under the pressure P be forced through the capillary and the observed time be t_1, and if then the same volume of fused salt be forced through the same capillary in the time t_2 under the same conditions except that of temperature, then it follows from (1) that

(2) $$\frac{\eta \text{ salt at } T_1^0}{\eta \text{ water at } T_2^0} = \frac{\text{time of salt}}{\text{time of water}} = \frac{t_1}{t_2}$$

except for such corrections as may be introduced by the expansion of the apparatus between T_2^0 and T_1^0. Since η for the water is known, η for the salt can be calculated.

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[1]) Pouisseuille, Mém. de l'Inst., 9, 1846.

The above assumes a sufficiently long capillary, so that formula (1) is valid. This means that pressure, length and radius, must have relative values within certain limits, that is, for a given pressure and length of capillary, its radius must not exceed a certain value etc. However, since from experimental reasons the length of the capillary must not be too great, nor its radius too small, it is important that the allowable magnitudes be discussed, that they may not be exceeded in one direction or the other. Hagenbach[1]) has shown that Pouisseuille's empirical formula can be deduced mathematically, making certain assumptions, and hence if the apparatus be designed so that these assumptions be realized physically, formula (2) may be used. To determine these assumptions, and to get an idea of what η signifies physically, the following mathematical discussion is undertaken. It is in principle that due to Hagenbach, only modified and shortened to be applied to the proper dimensioning of the apparatus to give results of a given degree of accuracy.

Mathematical Discussion of Pouisseuille's Formula, Applied to Dimensioning Apparatus

The following deduction applies to a horizontal cylindrical capillary which is wet with the liquid at the time of commencing the experiment. The liquid as it passes through the capillary may be considered as a system of coaxial hollow cylinders, moving with decreasing velocity as they approach the walls of the capillary. The outer cylinder against the capillary, simply

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[1]) Hagenbach, Pogg. Ann. CIX.

wets the wall and moves with zero velocity. Hence any elementary hollow cylinder has a faster moving next inward lying layer, which tends to accelerate its motion, and a slower moving next outward lying layer, which tends to retard its motion, due to their friction.

If u is the velocity of a layer distant x from the centre, and u + du that of the layer distant x + dx from the centre, where dx is the effective distance between two molecular layers, then the force retarding the faster moving layer, which is proportional to their difference in velocity, equals

(3) $$K = e \, S \, du$$

when S is the surface of contact of the two layers, and e a constant depending upon the material. In this form e cannot be determined since du and similarly dx are unknown. To get around this, the coefficient of internal friction is not defined as e, but as follows. The velocity of any hollow cylindrical layer is a function of its distance from the centre,

$$u = f(x)$$

hence
$$du = \frac{du}{dx} \, dx$$

which substituted is (3) gives

$$K = \left(e \, dx \right) \frac{du}{dx} \, S$$

Since dx depends only upon the molecular dimensions, (e dx) is a constant depending only upon the material, and this is what is defined as the coefficient of internal friction η, hence

(4) $$K = \eta \, S \, \frac{du}{dx}$$

It follows, that the coefficient of internal friction is the force acting on unit contact surface of two layers of the liquid, when there is unit difference in velocity between two layers unit distance apart.

η is of the dimensions $\left[\begin{array}{cc} -1 & -1 \\ cm & grm \ sec \end{array}\right]$

Equation (4) admits of numerical calculation if two assumptions be made:—1) that the velocity of flow of the liquid through the capillary be uniform 2) that there be no external work done as the liquid leaves the capillary. In this case the acceleration which the force applied tends to impart to any layer must just equal the difference between the acceleration and retardation which it suffers from its two neighboring layers, and which are given by expression (4). Writing this equality for an elementary hollow cylinder of length dl, where l is its distance from one end of the capillary, and of thickness dx, where, as before, x is its distance from the centre of the cylinder, there results, neglecting differentials of higher orders,

$$(5) \qquad \frac{dp}{dl} = \frac{1}{x} \left\{ \frac{du}{dx} + \frac{d^2u}{dx^2} \right\} \eta$$

p is the pressure at the point distant l from the end, and u is the velocity of a layer distant x from the centre.

Since the left hand member of (5) is independent of x, and the right hand member independent of l, each may be placed equal to a constant, and integrated. There results

$$(6) \qquad u = \frac{P}{4 \ \eta \ L} (R^2 - x^2)$$

where P is the difference in pressure between the ends of the capillary, L is its length, and R its radius. u is then, the velocity of a hollow cylinder of base $2 \pi x \, dx$; hence the volume flowing through the capillary in unit time, due to this layer, is $u \cdot 2 \pi x \, dx$, and the total volume flowing through the entire capillary in the time t, is

$$V = \int_0^R u \cdot 2 \pi x \, dx \cdot t$$

which from (6) gives

$$V = \frac{2 \pi t P}{4 \gamma L} \int_0^R (R^2 - x^2) \, x \, dx$$

or (7) $\quad V = \dfrac{1}{\gamma} \dfrac{\pi}{8} \dfrac{P}{L} R^4 t$

which is Pouisseuille's formula.

Hence the capillary must be so chosen, and the pressure applied must be of such magnitude, that the liquid flows with a uniform velocity, and does no external work upon leaving the capillary. This last condition can only be approximated to, but for an allowable error of $0,1\,\%$ the relative dimensions of the apparatus can be found as follows.

The mass of liquid flowing through the elementary hollow cylinder with velocity u, in the time t, is

$$dm = s \, 2 \pi x \, dx \, u \, t$$

where s is the specific gravity of the liquid. Its kinetic energy, as it leaves the capillary, is from (6)

$$\tfrac{1}{2} \, dm \, u^2 = \tfrac{1}{2} \, (s \, 2 \pi x \, dx \, t) \left\{ \frac{P}{4 \gamma L} (R^2 - x^2) \right\}^3$$

$$= \frac{P^3}{(4 \gamma L)^3} \, \pi \, s \, t \, (R^2 - x^2)^3 \, x \, dx$$

and the total kinetic energy as the liquid leaves the capillary is

$$h = \frac{P^3}{(4 \, \eta \, L)^3} \, \pi \, s \, t \int_0^R (R^2 - x^2)^3 \, x \, dx$$

$$= \frac{P^3 \, \pi \, s \, t \, R^8}{2 \cdot 4^4 \, \eta^3 \, L^3}$$

which from equation (7) gives

$$h = \frac{V^3 \, s}{\pi^2 \, t^2 \, R^4}$$

But the total energy applied is PV, hence the fractional part used in doing external work is

$$\partial = \frac{V^2 \, s}{\pi^2 \, t^2 \, R^4 \, P}$$

and for an allowable error not to exceed 0,1 % we have

(8) $$\frac{V^2 \, s}{\pi \, t^2 \, R^4 \, P} < \frac{1}{1000}$$

In performing the experiment the pressure can be kept constant to within 0,2 mms. of mercury, hence for an accuracy of 0,1 %, a pressure not less than 20 cms. of mercury must be used. This fixes the limit for the value of P. It is difficult to obtain good capillaries of suitable hard glass with a radius of less than 0,07 mms., and again beyond this limit the slightest trace of dust interferes with the experiment. For sodium nitrate (s) is approximately 1,8. Hence from (8) the length of the capillary must be such, that the volume flowing through it per second is less than

$$\frac{V}{t} < \sqrt{\frac{\pi^2 \cdot ,007^4 \cdot 20 \cdot 13,6 \cdot 960}{1,8 \cdot 1000}} < ,0017$$

c. cms. per second. With the apparatus used for sodium nitrate, the data (pp. 46) shows that it took 953,5 seconds to fill a volume of approximately 1,6 c. c., or

$$\frac{V}{t} = \frac{1,6}{953} = ,0017$$

which is just within the limit.

The final test to which each capillary apparatus was put before using it for measurements, was to determine the absolute coefficient of water with it. This was done as follows. The radius of the capillary was determined by filling it with a mercury thread and weighing the mercury. From the length of the capillary, which could be measured directly, and from the density of mercury under the conditions of the experiment, the radius was calculated. Similarly the volume v up to the mark m (figure 3) was measured, by filling it with mercury and weighing. Then water at 13° was forced through the capillary under the known pressure P, and the time required to fill the volume v accurately observed. Then all the factors in Pouisseuille's formula are known, from which to calculate η. A capillary was of sufficient length, when the value of η as calculated from this measurement, did not vary from ,01203 by more than 2 units in the last place of figures. This is the mean value of the determinations of η for water at 13°, by Gartenmeister, Heydweiller, Noack, Pacher, Pouisseuille, Slotte, Sprung, and Thorpe and Rodger. My own observations with an excessively long capillary gave ,01202. It is clear that if the capillary be longer than necessary, the time of flow increases correspondingly, and the accuracy of the temperature measurements decreases.

Viscosity; Apparatus and Measurements

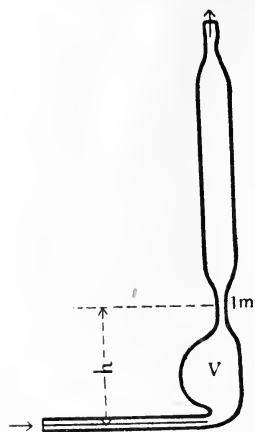The form of the capillary tube is shown in figure 3. The length of the capillary varied from 4 to 10 cms. and its radius from ,006 to ,01 cms. The volume v was from 1,5 to 3 c. c., and the height h about 4 cms. The tube was drawn very thin at m where a fine line was scratched so that at the instant the liquid reached the mark, the time could be accurately recorded, that is, so that the error in the volume would be a minimum.

This apparatus was connected through a heavy rubber tube, fitted with a cock, to a large air reservoir, which was kept evacuated to the desired pressure by means of a Bunsen water pump. A mercury manometer was connected to the reservoir from which the difference between atmospheric pressure and the pressure of the reservoir was read.

Fig. 3.

The experiment was carried out as follows. The salt within the electric oven had been heated to the desired temperature, and the pump was operated until the required manometer reading was observed. The bulb of the capillary tube was put in connection with the reservoir by opening the cock. Air was drawn in through the capillary at such a slow rate due to its fineness, and the reservoir was so large, that the change in pressure from this source, and from leakage

throughout the whole system was compensated by a very moderate pressure of water at the pump. Once in equilibrium very little regulation was necessary, and by watching the manometer carefully throughout the experiment, and by changing the water pressure slightly as required, it was possible to maintain the pressure constant to within 0,2 mms. Then the capillary was inserted within the melted salt almost to the mark m, and at the instant the capillary touched the liquid the time was recorded. With practice this could be done to within 0,5 sec., which is equally true of the final time observation, and as the time interval was usually over 500 secs., the error introduced was very small. Galvanometer readings were made every $1/2$ minute, and from the mean of these the temperature was calculated as shown on pp. 46 etc. These readings never varied over an amount corresponding to more than a degree, so that the mean corresponded very closely to the true temperature. The pressure was kept constant during the experiment until the salt just rose to the mark m, at which instant the time was again accurately recorded. At this point the tube leading to the reservoir was quickly removed, to prevent the salt from rising beyond the limits of the melt where it would freeze out. A second rubber tube was then connected to the capillary apparatus leading from a small carbondioxide bomb. The pressure from this was used to force the salt out of the capillary apparatus, while it was still within the melt. When empty the apparatus was removed, cooled, cleaned and the entire operation repeated.

This same measurement was carried through with

water at 13°, and the results compared according to formula (2), subject to the following corrections.

Correction for the Expansion of Glass

The length and radius of the capillary, as well as the volume of the bulb (v. figure 3), will be different at the temperature of the water determination, from what they are at the temperature of the salt determination. This correction was spoken of on pp. 5 in connection with Foussereau's work, and it remains to show that its magnitude is zero. From formula (1)

$$\eta = \left(\frac{\pi}{8} P t\right) \frac{R^4}{L V};$$

it follows, that at a given temperature and pressure, η is proportional directly to the 4th power of the radius, and inversely to the length of the capillary and the volume of the bulb. If the lineal coefficient of expansion of glass be α, the difference in temperature causing the radius to increase will increase η proportional to α^4. Similarly the difference in temperature will cause L and V to expand proportional to α and α^3 respectively, or due to the two together, η will diminish proportional to α^4. Hence the effect of the expansion of R, making the liquid pass more readily, is just offset by the effect of increased volume and length, causing an increased time of flow, and the total effect is zero.

Correction for the Pressure of Liquid

The pressure forcing the liquid through the capillary is the difference between atmospheric pressure and the diminished pressure of the reservoir, which differ-

ence was read from the manometer, plus the pressure due to the acting column of salt itself. This latter, which may be looked upon as a correction to the manometer reading, is

$$C = \frac{1}{2} \, h \, s \, g$$

where h is the distance from the capillary to the scratch m (fig. 3), that is, where $\frac{1}{2}$ h is the average height of the acting column of salt during the experiment, where s is the specific gravity of the salt, and g the acceleration due to gravity. The magnitude of this correction may be seen from the following. The smallest value of P used was 15 cms. of mercury. This was for measurements with sodium nitrate having a specific gravity of approximately 1,8. Hence, since h is about 4 cms.

$$\frac{C}{P} = \frac{\frac{1}{2} \, . \, 4 \, . \, 1,8 \, . \, 980}{15 \, . \, 13,6 \, . \, 980} = .018$$

For the same measurement with water

$$\frac{C}{P} = \frac{\frac{1}{2} \, . \, 4 \, . \, 1 \, . \, 980}{15 \, . \, 13 \, . \, 980} = ,010$$

Thus the magnitude of the correction is 0,8 %. This correction is made throughout the calculations, but it is evident that only an approximate value of the specific gravity of the salt is required.

Viscosity; Calculation and Results

A single illustrative calculation will be carried out completely from the original data. For sodium nitrate, while the bulb was being filled under a manometer pressure of 15 cms. of mercury, the following galvanometer readings were made, at $1/2$ minute intervals.

1	9,04	9	9,05	17	9,05	25	9,02
2	9,04	10	9,06	18	9,05	26	9,02
3	9,04	11	9,06	19	9,04	27	9,02
4	9,05	12	9,06	20	9,04	28	9,01
5	9,06	13	9,06	21	9,04	29	9,01
6	9,05	14	9,06	22	9,03	30	9,01
7	9,05	15	9,06	23	9,03	31	9,01
8	9,05	16	9,05	24	9,03	32	9,01

mean $G = 9,04$.

From this mean value, and from readings with the normal Weston element etc., as described under temperature measurements, the temperature was calculated. The temperature corresponding to $G = 9,04$ is $351°$. The time required for the salt was $953 1/2$ seconds, and for water under the same manometer pressure of 15 cms. of mercury, and at a temperature of $13°00$, the time required was 480,0 secs. Pouisseuille's formula says

$$\eta_s = \frac{1}{V} \frac{\pi}{8} \frac{R^4}{L} P_s \, t_s$$

and
$$\eta_w = \frac{1}{V} \frac{\pi}{8} \frac{R^4}{L} P_w \, t_w = ,01203$$

or $\eta_s = ,01203 \dfrac{P_s\, t_s}{P_w\, t_w}.$

P_s is the manometer pressure, plus the correction for the pressure of the acting column of salt (pp. 44) or

$$P_s = 15,0 \ . \ 13,6 \ . \ 980 + \text{\textonehalf} \ . \ 4 \ . \ 1,8 \ . \ 980$$
$$= 207,6 \ . \ 980$$

Similarly $P_w = 15,0 \ . \ 13,6 \ . \ 980 + \text{\textonehalf} \ . \ 4 \ . \ 1,0 \ . \ 980$
$$= 206,0 \ . \ 980$$

Hence for sodium nitrate at $351°.[1])$

$$\eta = \frac{,01203 \ . \ 207,6 \ . \ 980 \ . \ 953,5}{206,0 \ . \ 980 \ . \ 480,0}$$
$$= 0,02408$$

In this way values of η were calculated for repeated observations made at temperature intervals of from 5 to 10 degrees, and the results plotted. The points lay along a smooth curve. From this curve, which represents the mean of the entire series of observations, the values of η for 10 degree intervals, beginning at the melting point, were read, and these values are tabulated below. The deviation of the results from the mean, at points where a number of observations were made at the same temperature, are slightly greater than for the conductivity measurements, being usually from 0,4 % to 0,5 %.

The following tables are then, the mean values of the coefficient of internal friction as observed, given for $10°$ temperature intervals, commencing with the melting point. In addition, the 3rd column gives the increase in the coefficient for the corresponding $10°$,

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[1]) See pp. 48, column 2.

the 4th column gives the specific conductivity X, from the tables pp. 32 etc. and the 5th column gives the product of the specific conductivity and the coefficient of internal friction at the corresponding temperature.

Sodium Nitrate

T	η	$\triangle$	X	$X \eta \, 10^4$
308	.02919		0,965	282
		.0132		
318	.02787		1,022	284
		.0126		
328	.02661		1,065	285
		.0119		
338	.02542		1,108	283
		.0103		
348	.02439		1,151	280
		.0105		
358	.02334		1,195	278
		.0097		
368	.02237		1,239	276
		.0095		
378	.02142		1,283	275
		.0085		
388	.02057		1,327	273
		.0080		
398	.01977		1,371	271
		.0077		
408	.01900		1,416	269
		.0072		
418	.01828		1,461	268

Potassium Nitrate

T	η	$\triangle$	X	$X \eta \, 10^4$
333	.02970		.6060	180
		.0140		
343	.02830		.6454	183
		.0137		
353	.02693		.6759	182
		.0130		
363	.02563		.7040	180
		.0121		
373	.02442		.7320	178
		.0115		
383	.02327		.7600	177
		.0111		
393	.02216		.7880	175
		.0107		
403	.02109		.8160	173
		.0102		
413	.02007		.8440	173

Potassium Bichromate

T	η	$\triangle$	X	$X \eta\, 10^4$
397	.1339		.1959	251
		.0080		
407	.1259		.2198	263
		.0072		
417	.1187		.2381	282
		.0066		
427	.1120		.2563	288
		.0062		
437	.1059		.2745	290
		.0061		
447	.0998		.2927	292
		.0060		
457	.0938		.3109	292
		.0059		
467	.0879		.3291	288
		.0056		
477	.0823		.3473	283
		.0055		
487	.0768		.3655	281
		.0053		
497	.0715		.3837	275
		.0051		
507	.0664		.4019	267

Lead Chloride

T	η	$\triangle$	X	$X \eta\, 10^4$
498	.05532		1,395	770
		.00471		
508	.05061		1,478	748
		.00401		
518	.04660		1,544	721
		.00360		
528	.04300		1,596	687
		.00280		
538	.04020		1,645	661
		.00235		
548	.03785		1,692	651
		.00197		
558	.03588		1,738	642
		.00170		
568	.03418		1,783	610
		.00136		
578	.03282		1,826	600
		.00117		
588	.03165		1,866	591
		.00108		
598	.03057		1,904	582
		.00101		
608	.02956		1,941	573

Lead Bromide

T	η	$\triangle$	X	$X \eta\, 10^4$
372	.1019		.5397	550
		.01390		
382	.08800		.6115	537
		.00740		
392	.08060		.6479	520
		.00590		
402	.07470		.6842	510
		.00500		
412	.06970		.7202	502
		.00435		
422	.06535		.7557	491
		.00402		
432	.06133		.7900	484
		.00388		
442	.05745		.8239	473
		.00361		
452	.05384		.8570	452
		.00349		
462	.05035		.8900	448
		.00335		
472	.04700		.9220	433
		.00320		
482	.04380		.9530	417
		.00307		
492	.04073		.9835	400

CONCLUSION

A study of the x η column above, shows that in general this product drops with increasing temperature, that is, just as Hosking and others found for aqueous solutions, the viscosity falls off more rapidly than the conductivity increases. For sodium and potassium nitrates this product drops about $4^1/_2$ % per 100°, while for lead chloride it falls 24 % and for lead bromide 22 %. This in no sense confirms Foussereau's conclusion that the x η product is constant for all temperatures. Even in the case of the nitrates, for which this decrease is the least marked, and from which he based his conclusion, the x η values drop so regularly that the differences cannot be refered to experimental errors.

I have been unable to find any simple relation between the values of this product for the different salts, either by refering the measurements to chemically equivalent weights, to molecular volumes, or to any other comparative measures.

The specific conductivity and the viscosity may be expressed in terms of the temperature, according to the formulae

$$x = a + b t + c t^2 + -$$
$$\eta = \alpha + \beta t + \gamma t^2 + -$$

developing only to the second power, as these curves

do not depart widely from straight lines. The constants in these equations show no simple relations, that is, the conductivity and fluidity do not become zero at the same temperature for a single salt, much less for all salts, as was found for solutions by Kohlrausch and by Hosking. Much weight cannot be laid upon this conclusion however, as it is necessarily a process of extrapolation over a considerable range.

The explanation of the drop in the $x\eta$ column may be as follows. The conductivity of the salt is proportional to the concentration of its ions, and to their velocities. For solutions this is expressed by

$$x = c\,\alpha\,(u + v)$$

where c is the concentration of the solution, α its dissociation and $u + v$ the mobility of the ions. The mobility of the ions is a function of the viscosity of the medium, hence—

$$x \cdot f(\eta) = c\,\alpha$$

which as soon as $f(\eta)$ is determined by mobility measurements, gives a method of determining the dissociation of fused electrolytes α, which has hitherto been impossible. If we assume the mobility of an ion to be inversely proportional to the viscosity constant, which is a very rational assumption,[1]) we get

$$x\eta = K c\,\alpha.$$

c, the concentration, is proportional to the density, and since the density decreases with rising temperature, the $x\eta$ product must do likewise, unless the increase in α is just sufficient to offset this, which is highly impropable.

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[1]) See H. Euler, Zeitschr. f. Phys. Chem., 25, 1898.

So far as the establishment of the data of the specific conductivity of the fused salts is concerned, my results cannot be said to agree closely with any of the previous work done. It more nearly confirms that of Poincaré than that of any other investigator. If Poincaré's temperature measurements be considered wrong, which the more recent melting point determinations make very probable, and his data be compared with mine at equal intervals from the melting points, the agreement is a very fair one. The measurements of viscosity are for the most part entirely new. It seems quite out of the question that any of the above results should contain errors at all comparable with the differences between them and much of the existing data.

This work was carried on in the Electro-Chemical Laboratory of the Eidgenössischen Polytechnikum in Zürich, during the winter and summer semestres 1905-6, at the suggestion of, and under the direction of Prof. R. Lorenz. I take this opportunity to express my hearty thanks to Professor Lorenz, for the enthusiasm and interest which he has had at all times in the progress of the work, and for the kindly assistance which he has always been ready to lend.

Just as this work is completed, there appears a paper by K. Arndt, Zeitschr. f. Elektrochemie, May 1906, in which he describes measurements of the specific conductivity of some alkali chlorides and sulphates above 800°. He uses an ordinary U tube of porcelain, which material Poincaré and others have shown to have a considerable conductivity at those high temperatures.

Moreover, his cell had a resistance of only 5 to 10 ohms, with electrodes of 14 mms. diameter, which, from the discussion above (pp. 11 etc.), makes it doubtful that a high degree of accuracy could have been obtained. His measurements do not include any of the ones I have made, hence no comparisons can be drawn.